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A general discussion of the polymer pyrolysis route to ceramics – what it is, why it is important, and the chemical considerations that are important in its implementation – is followed by some recent examples from research at MIT involving polysilazane and polysilane chemistry.

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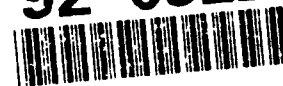
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SYNTHESIS AND USEFUL REACTIONS OF ORGANOSILICON POLYMERIC PRECURSORS FOR CERAMICS

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Inorganic and organometallic polymers are macromolecular systems in which the polymer backbone contains elements other than the carbon, oxygen and nitrogen usually found in organic polymers [1]. To take as an example silicon-containing polymers, in the silicones the polymer backbone is composed of the Si-O repeat unit; in polysilazanes, of the Si-N unit; in polysilmethylenes, of the Si-C unit. In the polysilanes there are only silicon atoms in the polymer backbone. Many of the other metalloids and metals among the elements in the Periodic Table have been or, in principle, can be incorporated into polymeric systems, so it is clear that the field of inorganic and organometallic polymers is a very large one. Inorganic and organometallic polymers have been of interest to chemists for a long time. It was the commercial development of the silicones in the 1940's that gave this field of research its modern impetus [2]. Once it was appreciated how useful these versatile organosilicon polymers could be, chemists became interested in the possibility of developing other organometallic (and also inorganic) polymers, ones that might complement or even surpass the silicones as far as useful applications were concerned. Research on inorganic and organometallic polymers became very active in the 1950's and 1960's. Work in this area became an international effort, prompted by the need for new materials that would meet the exacting demands of the jet age that had effectively commenced around the end of World War II. Even greater demands, in terms of materials that would still be useful under extreme conditions, came with the space age.

Inorganic and organometallic polymers were not unknown before the 1940's. Polymers of the type $(R_2SiO)_n$ had been prepared by Kipping and his students during the period 1910-1935, but their potential importance in terms of useful applications was not recognized. Some organometallic polymers went unrecognized as such for a long time: it must be remembered that macromolecular chemistry is a relatively new field. Thus the dialkyltin oxides were first prepared in 1854, but their polymeric nature was not recognized until nearly one hundred years later [3]. The research on inorganic and organometallic polymers carried out in the 1950's and 1960's covered a broad range: other organosilicon polymers such as the polysilazanes; polymetalloxanes; various boron-containing polymers including those derived from the very stable carboranes; polyphosphazenes; coordination polymers; metal-containing polyesters, polyamides and vinyl polymers. In all of these investigations it was the polymer per se that was of interest. The objective in most cases was a polymeric material whose properties at extremes of temperature would surpass those of the conventional organic polymers. High thermal stability was the main goal. Other properties, of course, were of interest: elasticity at low temperature, adhesion, flexibility, lubricity, resistance to aviation fuels, resistance to oxidation and other forms of chemical attack, and others. Although a few potentially useful materials were developed in these years, for instance, the new generation of polyphosphazenes [4] and the poly(carboranylenesiloxanes) [5], for the most part the yield of all this research in terms of useful inorganic or organometallic polymer systems was negligible.

The picture changed again in the 1980's when ceramics as potential replacement materials for metals and metallic alloys in many applications and also as "high technology" materials with completely new applications began to attract worldwide attention [6]. While much effort was and still is devoted to improving the reliability of ceramic components made from oxide and non-oxide ceramics by innovations in ceramics processing, it was the development of composites that has driven ceramics technology to new levels [7]. Composites that consist of one or more reinforcing materials (glass fibers, carbon fibers, ceramic fibers, etc.) in a matrix (polymer, metal, glass, ceramic, etc.) have greater strength and toughness than the matrix material alone and are finding wide applications in the aerospace industry. Composite materials can be fabricated that are lighter in weight and have higher strengths than many metals. Since ceramics have high thermal stability but are inherently brittle materials, it was the anticipated benefits of fabricating components from ceramic-ceramic composites that has been the driving force behind the recent interest in ceramics as structural materials for use in harsh environments. However, prior to

1980 there were few reinforcing materials commercially available for fabricating ceramic-ceramic composites, and those that were available did not meet the high-temperature requirements for some desired applications. It is in the area of composites that inorganic and organometallic polymers find many new and important applications. But these applications are not ones involving the polymers themselves, but rather, in the end, of their pyrolysis products, ceramic materials. Hence after synthesis come pyrolytic decomposition and conversion to a ceramic. This leads to the name "preceramic polymer" [8].

Complex ceramics processing issues must be addressed in the manufacture of strong continuous fiber ceramic matrix composites. It is beyond the scope of this brief article to discuss these; our focus is on the inorganic and organometallic preceramic polymers. In continuous fiber composites the ceramic fibers may be present in the form of filaments that usually are positioned unidirectionally, bidirectionally or multidirectionally in a ceramic matrix. Among the fabrication techniques that may be used for such ceramic matrix composites are hot pressing, chemical vapor infiltration, reaction bonding and polymer infiltration/pyrolysis. Thus the inorganic or organometallic polymer can play a role as the precursor for both the fiber and the matrix. Such polymers can, in principle, find another important use in the fabrication of continuous fiber ceramic matrix composites. To achieve optimum strength and toughness, there must be only weak, controlled chemical interaction between the fibers and the matrix material. To prevent strong fiber-matrix bonding, the fibers may have to be coated with a material that does not interact chemically with the matrix. Such coatings can be applied on the fibers by chemical vapor deposition, but they also can be formed by pyrolysis of a polymer coating on the fiber.

Finally, there is the problem of carbon/carbon composites, whose superior strength and thermal stability make them prime candidates for many "high tech" structural applications, but whose high temperature applications are compromised in the atmosphere by their ready oxidation. Here also, inorganic and organometallic preceramic polymers can find an important application. If pyrolysis of the polymer leads to a refractory and chemically inert ceramic, especially one that is stable to oxidation at high temperatures, then infiltration of the pores of the carbon/carbon composite and coating of its surface with this polymer, followed by pyrolysis, should give a protective coating that will allow use of the carbon/carbon composite with full benefit of its inherently high strength and thermal stability under otherwise hostile conditions. The use of polymer-derived ceramics to protect other surfaces such as those of reactive metals against chemical corrosion or oxidation at high temperatures also is a possibility. Such ceramic coatings, as formed by polymer pyrolysis, also can serve to strengthen the material they are coating.

A further application of inorganic and organometallic preceramic polymers of potential commercial importance is found in the area of conventional ceramic processing: in their use as binders in ceramic powder processing. Binders are used primarily to help ceramic powder particles adhere to one another. Both the green strength of a ceramic body and its green density are affected by the binder used. Although many types of materials have been employed as binders in ceramic powder processing, organic polymers, such as, for instance, polyvinyl alcohol, polyvinyl butyral, polyethylene and poly(methyl methacrylate), traditionally have played an important role in binder formulations [9]. While the use of such materials as binders often results in achievement of high green body strength and/or high green body density, there also can be some drawbacks associated with their use. Major problems can be encountered upon firing of the ceramic body due to binder burnout. Cracking of the part can result when the temperature range of the binder decomposition is narrow, so that most of the volatiles produced in its pyrolysis are released practically simultaneously. Furthermore, binder burnout can contribute to formation of voids in the microstructure of the final ceramic body. Such voids, which also can result from poor packing of the ceramic powder particles, can act as stress concentrators, and thus facilitate catastrophic failure. Usually, but not necessarily always, a drawback is that during the non-oxidative firing of the ceramic body there can be substantial retention of carbon, either due to incomplete polymer binder pyrolysis (giving nonvolatile carbonaceous residues) or due to polymer-ceramic surface bond formation which prevents degradative volatilization of the binder. In order to avoid these problems, ceramists more recently have become interested in "low loss" inorganic or organometallic polymeric binders. The polymers of choice are those whose pyrolysis gives a high yield of ceramic residue with release of a minimum quantity of potentially destructive volatiles. Preferably, this ceramic residue also will be the same material of which the powder is composed, but this is not an essential requirement. It can be a different material but still a useful one: to control sintering or grain boundary chemistry. By use of such "low loss" binders one may hope to achieve not only the desired high green body strength and density that
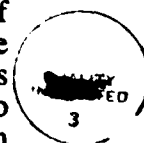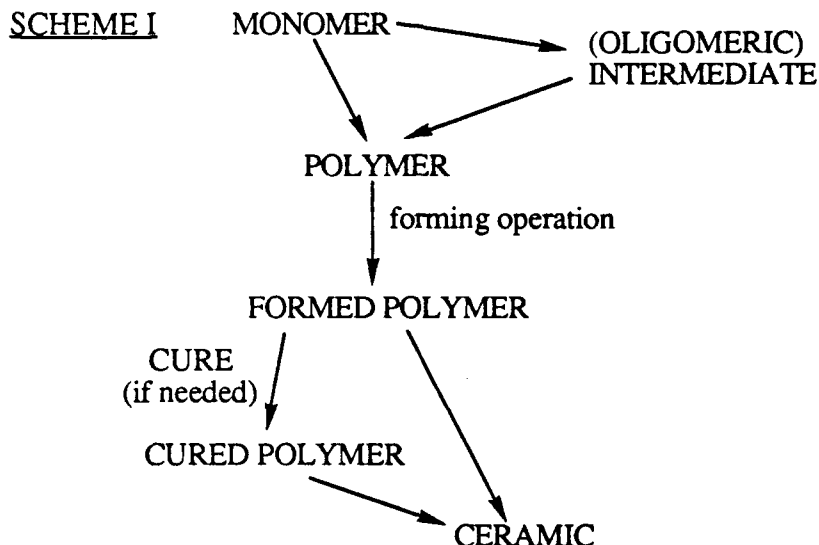
use of organic binders brings, but also one may hope to obtain ceramic parts of high strength and density. To date, most "low loss" organometallic binders that have been investigated have been organosilicon polymers. These are used as binders for silicon carbide and silicon nitride powders.

Let us now consider the preparation of preceramic polymers and the requirements in terms of their chemical and physical properties that must be met. Scheme 1 brings a simple flow-diagram of the processes involved in the preparation and utilization of a preceramic polymer. Chemistry, it may be noted, plays an important role in all steps.

SCHEME I

MONOMER ⟶ (OLIGOMERIC) INTERMEDIATE

POLYMER

forming operation

FORMED POLYMER

CURE (if needed)

CURED POLYMER

CERAMIC

First and foremost, the preceramic polymer must be processable. All of the applications discussed above require a polymer that is soluble in an organic solvent and/or meltable, so that it can be spun into fibers, formed into a coating by various means, infiltrated into a fiber preform or coated onto ceramic powder particles. Many known inorganic and organometallic polymers are immediately eliminated from consideration because they are intractable: neither soluble nor meltable. With others there is the problem that they are initially soluble in the reaction solution but, once isolated in the "dry" state after vacuum drying, they are no longer soluble, even in the reaction solvent. Obviously, further crosslinking can occur during concentration even when no heat is applied. Still other polymers may "age" on storage in the solvent-free state, becoming less soluble or even insoluble as a result of further slow crosslinking processes.

Another important requirement is that pyrolysis of the inorganic or organometallic preceramic polymer give as high a yield of ceramic residue as possible. Ceramic yields (= weight of ceramic residue x 100/weight of pyrolysis charge) of 60-75% are acceptable, but higher ceramic yields of 80% or greater are desirable. Most polymers that have an inorganic backbone contain substituents on some or all of the backbone atoms. These often are hydrogen atoms or organic groups, but they can be of other types. During the pyrolysis of the polymer these substituents may become incorporated into the ceramic residue or they may be eliminated in the form of volatile, low molecular weight compounds that escape as gaseous products at the high pyrolysis temperatures. Thus H and CH_3 are preferred substituents since their loss will leave a high ceramic residue yield (if the backbone atoms are retained). The pyrolysis of a polymer may give the theoretical yield of a ceramic as represented by the backbone atoms, but if the ceramic yield is low because of the large contributing weight to the pyrolysis charge of rather heavy substituents that will end up as volatiles, then useful applications of the polymer may be questionable. The high ceramic residue yield is of importance not from economic considerations. Rather, a high ceramic yield means that the quantity of gases evolved during pyrolysis will be small. These gases can be very destructive, especially if they are released over a narrow temperature range, causing cracking or even rupture of the ceramic part. So the fewer evolved gases, the better from the point of view of "good" ceramics. Lower ceramic yields, however, can be tolerated if the porosity generated in the developing ceramic during the pyrolysis is of the right kind: open porosity that lets the pyrolysis gases escape. Also, the greater the weight loss of a preceramic polymer on pyrolysis, the greater will be the shrinkage of the residual body. However, shrinkage is unavoidable when a polymer is pyrolyzed to a ceramic since one is

starting out with a material of low (1 g/cc or less) density and is forming a material of greater (2-3 g/cc) density.

The requirement of high ceramic yield on pyrolysis limits the types of polymers that will be useful precursors for ceramics. In general, linear, uncrosslinked polymers are not suitable since their pyrolysis leaves little if any solid residue. When pyrolytic scission of a bond in the backbone of a linear polymer occurs, small molecules usually are formed in subsequent steps. These, being volatile, are swept out from the hot zone by the carrier gas. What is needed is a crosslinked system, optimally a network polymer, so that if one bond breaks on heating, many bonds remain to hold the system together in the hot zone. While a substantial amount of crosslinking is desirable, it should not be so extensive as to cause gelation of the polymer. As noted above, a soluble system is required for the initial processing. The ideal preceramic polymer is one that is crosslinked but still soluble and that still contains reactive functionality ("latent reactivity", in the words of Wynne and Rice [8a]) that on heating will react to cause still further crosslinking to give the desired high ceramic yield. The design of a useful preceramic polymer thus requires the introduction of reactive functional groups at the monomer and/or polymer stage so that the initial stage of the pyrolysis results in formation of a highly crosslinked, nonvolatile, probably insoluble network, hence in retention of the elements of interest in the hot zone.

There are other requirements that must be met in order to have a useful preceramic polymer. There is the problem of elemental composition. At this point in the development of the chemistry of preceramic polymers, the preparation of very pure ceramics by polymer pyrolysis is not straightforward. It is not certain, in fact, what degree of purity is required for the applications enumerated above. In some cases, grossly impure systems will be unsatisfactory. For instance, in the case of the preparation of silicon carbide, SiC, by polymer pyrolysis, one would like to achieve a 1:1 ratio of Si to C in the ceramic product or, at the most, SiC plus only a small amount of free carbon, since carbon is a sintering aid for SiC. Depending on the precursor used, one might obtain on pyrolysis SiC plus a substantial amount of free carbon or SiC plus a substantial amount of free silicon (we have encountered both in our research). Neither alternative is acceptable. At the least, a large amount of free carbon in the ceramic product will bring problems of high temperature oxidation, but the free carbon could cause other, less obvious problems as well. On the other hand, a large amount of free silicon (mp 1414°C) would compromise the high temperature applications of the ceramic part. Effective control of the elemental composition of the final ceramic product can be achieved by manipulating the chemistry at the synthesis or even at the pyrolysis stage. In the synthesis of the preceramic polymer one can use appropriate mixtures of monomers so that pyrolysis gives a ceramic whose elemental composition is close to that desired. Alternatively, one can use a mixture of two polymers, in chemical or physical combination, so that pyrolysis gives the desired elemental composition. At this point, we cannot predict what elemental composition of the derived ceramic will be obtained on pyrolysis of a new inorganic or organometallic polymer, so it is for the most part a matter of doing experiments until pyrolysis trends are recognized. This empirical approach does work and in our own organosilicon chemistry we have been able to prepare preceramic polymers whose pyrolysis gives ~99% SiC, ~99.5% Si_3N_4, or any mixture of the two by appropriate manipulation of the chemistry.

The preparation of essentially pure silicon nitride by polymer pyrolysis represents a special case that illustrates another important chemical consideration: the choice of gas stream in the pyrolysis. Polymer pyrolysis usually is carried out in a furnace through which a gas is flowing. The gas stream serves two purposes: to protect the system from the atmosphere and to sweep away the volatiles produced in the pyrolysis. The gas used may be either an "inert" gas or a "reactive" gas. The pyrolysis of our polysilazane of composition $[(CH_3SiHNH)_a(CH_3SiN)_b]_n$ serves to illustrate the use of both types of pyrolysis gas stream [10]. Pyrolysis of this polysilazane in a stream of argon (an inert gas) to 1000°C gives a black ceramic residue in 80-85% yield. This material is amorphous, so composition in terms of pure species such as SiC and Si_3N_4 is meaningless. However, the analytical results (%C, N, Si) can be used to calculate a hypothetical composition in terms of SiC, Si_3N_4 and free C. The results of such a calculation in one case were: 67% by weight of Si_3N_4, 28% SiC and 5% C. This may be close to the actual composition of this material when it becomes crystalline above 1450°C. In marked contrast, when this polysilazane is pyrolyzed to 1000°C in a stream of ammonia, a white solid residue is obtained. This usually contains less than 0.5% by weight of carbon and is almost pure silicon nitride. The chemistry that takes place at temperatures of 400-600°C to remove the carbon must be complex. Reactions at these temperatures of the decomposing polysilazane with ammonia or

its decomposition products very likely are involved, but this question requires further study. We have used ammonia as the "reactive" gas to good advantage in the preparation of nitrides of other elements. For instance, polymers of the type $[B_{10}H_{12} \cdot \text{diamine}]_n$, where "diamine" may be ethylenediamine or its various N-methyl derivatives, piperazine, triethylenediamine or propylenediamine, when pyrolyzed in a stream of argon to 1000°C, give a black solid residue whose "composition" can be calculated from the elemental analysis as 1 B_4C + 1 BN + a minor amount of carbon. Pyrolysis in a stream of ammonia, on the other hand, results in formation of a white residue, essentially pure boron nitride, BN [11]. Similarly, pyrolysis of $(CH_3)_2N$-terminated $[Ti(NR)_2]_x$-type polymers in a stream of ammonia gives golden-yellow titanium nitride [12].

Little is known about the amorphous solids produced in the pyrolysis of inorganic and organometallic polymers. ^{29}Si solid state nuclear magnetic resonance studies of the pyrolysis product of a polysilazane that contains silicon, carbon and nitrogen, as reported by workers from the Dow Corning Corporation laboratories, suggested that in these materials the silicon atoms are randomly bonded to carbon and nitrogen atoms, rather than being in "islands" of SiC and Si_3N_4 [13]. Most of these amorphous ceramics crystallize when heated to 1400-1500°C and then, in the case of our polysilazane-derived amorphous silicon "carbonitride", X-ray diffraction lines due to α-Si_3N_4 and β-SiC are observed. The amorphous, porous, low density solids obtained in the pyrolysis of inorganic and organometallic polymers require further detailed study since in many applications it is these amorphous materials, not the crystalline materials that can be obtained from them, that are present. It may be noted that workers at the Ethyl Corporation have fabricated parts by compression molding followed by pyrolysis that were made from submicron SiC powder bonded with a polysilazane-derived amorphous silicon carbonitride matrix [14]. Bending strengths of up to 550 MPa and excellent oxidation resistance and strength retention at temperatures up to 1300°C were observed. The overall porosity in these parts was 20–25%.

As noted earlier, an important application of preceramic polymers is their use in the preparation of ceramic fibers. Most often, polymer fibers are spun from a melt of the the polymer (melt spinning). Alternatively, polymer fibers can be spun from a solution of the polymer into a hot chamber in which the solvent is flashed off, leaving the fiber (dry spinning) or into a nonsolvent in which the fiber coagulates (wet spinning). Of these, melt spinning is preferred: it gives the strongest green fibers and it avoids the use of large volumes of solvent that must be recycled. Preceramic polymers intended for melt spinning require a compromise. If the thermal crosslinking process is too effective at relatively low temperatures (100-200°C), then melt spinning will not be possible since heating will induce crosslinking and will produce an infusible material in the heated polymer-containing reservoir of the spinning apparatus prior to spinning. A less effective crosslinking process is needed so that the polymer forms a stable melt that can be extruded through the holes of the spinneret. The resulting polymer fibers, however, must then be "cured", i.e., rendered infusible, wholly or in part, so that the fiber form is retained on pyrolysis. Such cures may be effected chemically, most often by air oxidation or hydrolysis with moist air, but more complex chemistry can be applied. Such cures may also be effected by radiation, and ultraviolet, electron beam and gamma irradiation have been used. The radiation cures have the advantage that they do not introduce oxygen as do the oxidative and hydrolytic cures.

Another important requirement is that the polymer have the right rheological properties for the intended application. This is an important consideration when melt-spinnable fibers are desired, when thick or thin film coatings are to be prepared and when the preceramic polymer is to be used as a binder for ceramic powder formulations for injection or compression molding. In this connection, the ability to control the molecular weight of the polymer is important. A given molecular weight range will give rheological properties that may be satisfactory for one application but not for another.

Now that the main requirements for a useful preceramic polymer have been outlined, it will be of interest to consider some of the various inorganic and organometallic polymer systems that have been commercialized or whose commercialization is in the development stage. Although the possibility of preparing ceramics by polymer pyrolysis was first discussed by Aylett [15a] and by Chantrell and Popper in 1965 [15b], it was not until the mid-70's that the preparation of preceramic polymer fibers was reported. Verbeek of Bayer AG developed a precursor for Si_3N_4/SiC based on the reaction product of methyltrichlorosilane and methylamine, $CH_3Si(NHCH_3)_3$ [16]. Thermolysis of this compound at 520°C resulted in formation of methylamine and other volatile products and left a brittle, transparent, yellow-brown "carbosilazane resin" that was soluble in organic solvents. This polymer could be melt-spun at

220°C to give fibers, which after a moist air cure step, could be pyrolyzed at 1200°C to give glistening, black ceramic fibers in 55% ceramic yield. When they were heated to 1800°C, crystallization to β-SiC and α- and β-Si₃N₄ occurred. Another polymeric precursor for Si_3N_4/SiC ceramics, developed at about the same time by Winter, Verbeek and Mansmann at Bayer AG [21], was based on the reaction of $RSiCl_3$ compounds or of mixtures of R_2SiCl_2 and $RSiCl_3$ compounds with ammonia. The resulting polysilazane (usually with R = CH_3) could be used as a binder for SiC powder, or to form, after pyrolysis, ceramic films, and, with the help of an organic polymer as a spinning aid, ceramic fibers. This process was not commercialized, but it has provided the basis for much derivative work in other laboratories around the world.

An important early contribution to the area of preceramic polymers for silicon-containing ceramics was made by Yajima and his coworkers in Japan, who developed a process that results in the formation of ceramic fibers of high SiC content [18]. The initial step of this process is the sodium condensation of dimethyldichlorosilane, $(CH_3)_2SiCl_2$, in xylene solution to give an insoluble poly(dimethylsilylene), $[(CH_3)_2Si]_n$. This polymer is not a useful preceramic material: its pyrolysis gives a very low ceramic yield. However, when this polymer is heated in an autoclave at 450-470°C, complex chemistry takes place and a useful polymer that may be melt-spun is obtained. This material no longer contains an all-silicon backbone; the thermal treatment has caused extensive structural changes. Nuclear magnetic resonance (NMR) spectroscopic studies established that it has a complex structure, with one of the major components being the $CH_3(H)SiCH_2$ unit. The presence of the $(CH_3)_2SiCH_2$ unit also was established, but the fact that pyrolysis of this polycarbosilane gives a 55-60% ceramic yield suggests that a crosslinked structure is present. We note that pyrolysis of a linear $[(CH_3)HSiCH_2]_x$ polycarbosilane gives a ceramic yield of only 5% [19]. The representative part-structure shown in Figure 1 was
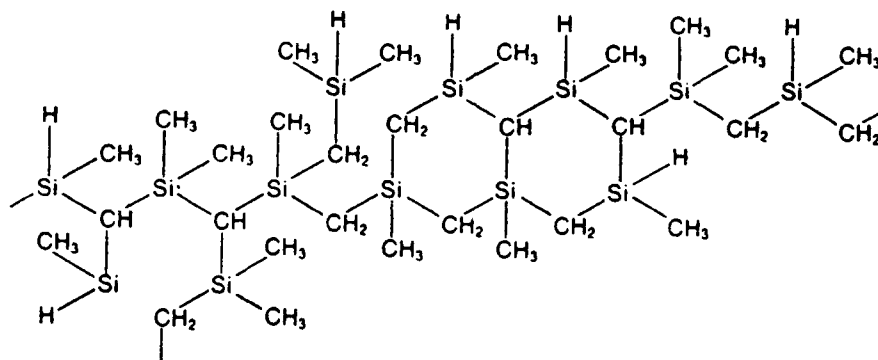

Figure 1. Constitutional chemical formula of polycarbosilane.

suggested by Yajima for his polycarbosilane. After this polycarbosilane resin had been melt-spun at around 350°C, the polymer fibers required a cure step before they could be pyrolyzed to ceramic fibers. This was effected by heating them in air at 190°C (but γ-irradiation also has been used to cure these fibers [20]). When the cured fibers were heated to 1200-1300°C in an inert atmosphere, "SiC" fibers were obtained. These were shown by analysis to contain an excess of carbon (over "SiC") and some oxygen. The analytical results could be translated into a "composition" of 1 SiC, 0.78 C, 0.22 SiO_2. The silica is derived from the air cure. Crystallization of the amorphous ceramic occurred above 1200°C. Above 1300°C gaseous CO was evolved and the strength of the ceramic fiber was lost. A variation of this basic procedure in which the thermal treatment of the initial polysilane was carried out at atmospheric pressure in the presence of a borosiloxane was developed as well. In another variation, the Yajima polycarbosilane was heated with a titanium alkoxide, $Ti(OR)_4$, to give a more highly crosslinked titanium-containing polymer. Pyrolysis of this product resulted in formation of a ceramic material that contained titanium carbide as well as silicon carbide.

The ceramic fibers obtained by the Yajima procedure are produced (trade name, Nicalon) by the Nippon Carbon Company, the titanium carbide-containing fibers (trade name, Tyranno) by Ube Industries. Many studies of the Nicalon fibers have been published and their use in the fabrication of ceramic, glass and metal matrix composites is well documented. There are various problems associated with the use of the Nicalon fibers at high temperatures and the search continues for ceramic fibers with better high temperature properties.

At the present time there is much research activity and some development effort in the area of preceramic polymer chemistry. This includes substantial industrial efforts, principally in the
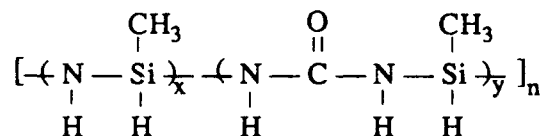
USA, Japan, France and Germany, as well as research in universities and research institutes around the world. Space does not permit a review of this work. The time required for a successful R&D effort in this area is long (probably a minimum of ten years) and successful commercialization requires close collaboration between the company that produces the preceramic polymer and the ceramic products derived from it and the end user. Compared to common high-volume polymers, preceramic polymers, in general, are expensive. At the present time, the end-users, in the main, are the aerospace companies and thus, for the time being, the market for such polymers is not a large one.

My research group at MIT has been active in the synthesis of preceramic polymers and their further modification to make them more useful. In our earlier work, we have developed useful polysilazanes [10] and silazanylborazines [21] by appropriate reactions of the mixture of liquid, low molecular weight cyclic oligomers (mostly trimer and tetramer) that are obtained in the ammonolysis of CH_3SiHCl_2. This chlorosilane is a by-product formed in the reaction of CH_3Cl with Si/Cu (which, as carried out in the silicones industry, gives mainly $(CH_3)_2SiCl_2$), so it is readily available and relatively cheap. We have been interested in still other chemistries that might convert the cyclo-$[CH_3Si(H)NH]_n$ oligomer mixture obtained from CH_3SiHCl_2 to materials of higher molecular weight that would be useful precursors for silicon carbonitride and silicon nitride.

A reaction of hexamethyldisilazane that is described in the literature [22] is shown in Eq. 1.

$$[(CH_3)_3Si]_2NH \ + \ O=C(NH_2)_2 \ \xrightarrow{\text{heat}} \ NH_3 \ + \ [(CH_3)_3SiNH]_2C=O \qquad (1)$$
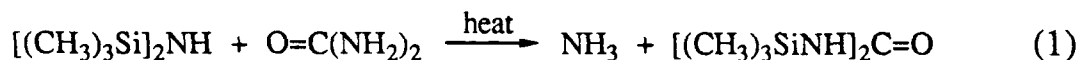
Such a reaction with urea, if applied to a cyclosilazane, e.g., the $[CH_3Si(H)NH]_n$ oligomers, should give polymeric products of type

$$[\!\!-\!\!(\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{N}}\!-\!\underset{\underset{H}{|}}{\overset{\overset{|}{Si}}{}}\!)_x\!-\!(\underset{\underset{H}{|}}{\overset{\overset{}{N}}{}}\!-\!\overset{\overset{O}{\|}}{C}\!-\!\underset{\underset{H}{|}}{\overset{}{N}}\!-\!\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{Si}})_y]_n$$

through ring-opening polymerization. Products more complicated than this would, however, be expected since organosilazane systems in general are thermolabile and the $[CH_3Si(H)NH]_n$ cyclic oligomers undergo crosslinking to some extent on being heated. In any case, reaction of four molar equivalents (as $CH_3Si(H)NH$) of $[CH_3Si(H)NH]_n$ oligomers with one of urea in pyridine at 85°C for 24 hr resulted in a white solid that was soluble in pyridine and THF but not in hydrocarbon solvents. ^1H NMR and IR spectroscopy established the presence of NH, CH_3, SiH and amide C=O functions. This product obviously must be a crosslinked polymer since the yield of ceramic residue obtained in a TGA experiment (10°C/min to 950°C in argon) was 83% (vs ~20% for the $[CH_3Si(H)NH]_n$ oligomer mixture). In a furnace pyrolysis (in argon to 1400°C), a 73% ceramic yield was obtained. Elemental analysis of the black ceramic residue showed 13.65% C, 29.67% N and 49.19% Si. The difference, 7.5%, may represent oxygen. The formation of a silicon oxycarbonitride thus is indicated.

Use of greater $CH_3Si(H)NH$/urea ratios gave polymers that were more soluble. Thus the 6:1 product was a white solid which was at least partially soluble in diethyl ether, benzene and chloroform, and the 10:1 product was a colorless gum that was soluble in diethyl ether and benzene but not in hexane. When the reaction was carried out with the $CH_3Si(H)NH$ unit and urea in 12:1 molar ratio, a liquid product was obtained, but the ceramic yield (by TGA) was 78%. Thus variation of the $CH_3Si(H)NH$/urea ratio results in changes in the physical nature of the polymer produced from solid to gum to liquid and so the rheological behavior of the product polymer also may be controlled.

As was the case with our other polysilazanes, pyrolysis of the $[CH_3Si(H)NH]_n$/urea products in a stream of nitrogen gave a white ceramic residue. For instance, when the 10 $CH_3Si(H)NH$/1 urea product was pyrolyzed in ammonia, the resulting ceramic contained 55.20% Si and 41.87% N and less than 0.5% C. Our studies relating to the more detailed characterization of this new system of polymers, to the course of their pyrolytic conversion and the characterization of the ceramic products are still in progress.

Another CH_3SiHCl_2-derived polymer that has been the subject of much attention in our laboratories, initially by T.G. Wood, is the polysilane obtained by sodium condensation of this chlorosilane. In this reaction, independently studied by Brown-Wensley and Sinclair [23], attack

at the Si–Cl linkages is preferred, but reaction can also occur at the Si–H bond. To what extent such attack at Si–H occurs is dependent on the reaction conditions used. For instance, a reaction of CH_3SiHCl_2 with an excess of sodium carried out in 7:1 (by volume) hexane/THF gives liquid products of composition (by NMR) $[(CH_3SiH)_x(CH_3Si)_y]_n$, with $x = 0.65 - 0.9$ and $y = 0.35 - 0.1$ and $n = 14-16$. Thus, between 10 and 35% of the Si–H bonds have reacted. This leads to some crosslinking since hydrogen loss generates trifunctional silicon atoms. These polysilanes are not good ceramic precursors. On pyrolysis to 1000°C the ceramic yield obtained from them ranged between 12 and 27% and the composition of the ceramic product (on the basis of elemental analysis) in one case was 1.0 mole SiC + 0.42 g atom Si. A better product, at least in terms of ceramic yield on pyrolysis, was obtained when the sodium condensation of CH_3SiHCl_2 was carried out in THF alone. As might be expected, the extent of reaction of the Si–H bond was considerably greater and the composition of the product was, on the average, $[(CH_3SiH)_{0.4}(CH_3Si)_{0.6}]_n$. That is, 60% of the Si–H bonds had reacted. As a result, the polymeric product was much less soluble in hydrocarbon solvents, but it was soluble in THF. The greater crosslinking also had as a useful consequence that the ceramic yield on pyrolysis to 1000°C was increased to 60%. However, the problem of the elemental composition of the ceramic residue remained, the composition being (on the basis of elemental analysis) 1.0 SiC + 0.49 Si. Such an excess of silicon (mp 1414°C) would be expected to compromise the high temperature applications of this ceramic material.

The $[(CH_3SiH)_x(CH_3Si)_y]_n$ polysilanes contain reactive Si–H and Si–Si functionality which should provide the basis for further chemical conversions which might serve to convert the at first sight unpromising polymers to useful preceramic materials. We have been successful in finding appropriate reactions of the $[(CH_3SiH)_x(CH_3Si)_y]_n$ polysilanes which served to deal with both the ceramic yield and ceramic composition problems. One approach used hydrosilylation reactions of the reactive Si–H bonds [10d,24]. Another was based on base catalyzed rearrangement of these polysilanes which increased the crosslinking and hence increased ceramic yields to 60% in the case of the liquid polysilane [10c-f]. When the base was a polysilazane that contained potassium amide functions, then the elemental composition problem could be dealt with successfully. In spite of these successful solutions to the ceramic yield and ceramic composition problems, we were interested in a simpler solution, one in which the additional chemistry required would be minimal. We have found such chemistry in the dehydrogenative coupling of organosilicon hydrides as developed a few years earlier by Aitken, Harrod and Samuel [25]. These workers had found that primary silanes $RSiH_3$ ($R = n-C_4H_9$ and C_6H_5) react to give oligomers with Si–Si bonds (polysilanes) in the presence of catalytic quantities of dimethylmetallocenes, $\underline{1}$, of the Group 4 metals Ti and Zr. Products of type $H(RSiH)_nH$ (n up

(M = Ti, Zr)
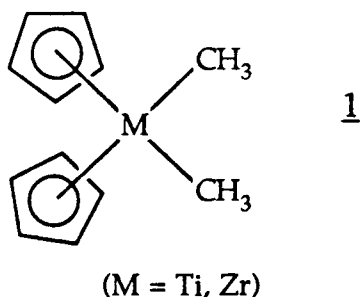
to 10 (Ti) and 20 (Zr)) were obtained and H_2 was evolved. It is noteworthy that such reactions work well only with primary silanes. Secondary silanes, R_2SiH_2, gave only dimers and trimers in low yield and tertiary silanes, R_3SiH, did not react at all. Later work by Harrod and others showed that cyclic as well as linear oligomers also were formed [25]. Nothing was known about the reactivity of polysilane hydrides toward such catalysts, and so we examined such systems, i.e., $[(CH_3SiH)_x(CH_3Si)_y]_n/(\eta-C_5H_5)_2M(CH_3)_2$ (M = Zr, Ti) and related catalysts. Our experiments have shown that $(\eta-C_5H_5)_2Ti(CH_3)_2$, $(\eta-C_5H_5)_2Zr(CH_3)_2$, as well as $[(\eta-C_5H_5)_2ZrH_2]_n$ and $(\eta-C_5H_5)_2ZrHCl$, are very effective catalysts for the crosslinking of the $[(CH_3SiH)_x(CH_3Si)_y]_n$ polysilanes [27]. Unexpected and surprising was the observation that in these catalyzed reactions of the $[(CH_3SiH)_x(CH_3Si)_y]_n$ polysilanes the ceramic residues obtained in their pyrolysis approached stoichiometric SiC in composition.

The Zr-based catalysts could be activated by heating or by ultraviolet (UV) irradiation. The titanium complex was effective even at room temperature. In a typical reaction using

$[(\eta\text{-}C_5H_5)_2ZrH_2]_n$ as catalyst, a mixture of liquid $[(CH_3SiH)_{0.68}(CH_3Si)_{0.32}]_n$ and the catalyst in hexane was heated at vigorous reflux (argon atmosphere). The initially insoluble catalyst dissolved and an orange solution resulted. After 2 hr, the solvent was evaporated under reduced pressure, leaving an air-sensitive orange solid in quantitative yield. Examination of the latter by ^{1}H NMR spectroscopy showed broad resonances at 0 - 1.1 (Si–CH$_3$) and 3.6 - 4.4 ppm (Si–H), as well as weak signals at 5.87 and 5.95 ppm due to η-C$_5$H$_5$Zr. Integration of the Si–CH$_3$ and Si–H signals established the composition $[(CH_3SiH)_{0.53}(CH_3Si)_{0.47}]_n$, i.e., there had been a loss of Si–H bonds. The ceramic residue yield (by TGA) had been increased from 24% for the base polysilane to 74%. A furnace pyrolysis to 1500°C in a stream of argon gave a black ceramic residue in 72% yield. Elemental analysis of the latter (29.89% C, 69.90% Si, 1.48% Zr, <0.5% H) allowed calculation of the composition (by weight) 98.0% SiC, 1.6% ZrC and 0.4% Si (vs. 74% SiC and 26% Si for the ceramic product of the pyrolysis of the base polysilane). Examination of the ceramic produced by XRD showed lines due to β-SiC (none for elemental Si) and two weak lines which could not be assigned.

When $(\eta\text{-}C_5H_5)_2Zr(CH_3)_2$ was used as catalyst (0.7 - 1.6 mol %), either heating at reflux in hexane solution for 2 hr or UV irradiation in hexane for 2 hr served to give crosslinked orange oils or solids whose pyrolysis gave ceramic residue yields in the 71-85% range. In one such reaction, a furnace pyrolysis as described above yielded a black ceramic residue of composition (via elemental analysis) 93.3% SiC, 5.6% ZrC and 1.0% Si (by weight). $(\eta\text{-}C_5H_5)_2ZrHCl$ also was a catalyst for crosslinking this polysilane, but it appeared to be somewhat less effective than the zirconocene hydride and methyl derivatives. However, high pyrolytic conversion to SiC could be achieved with this catalyst as well. In one experiment (0.9 mol % catalyst, reflux in toluene for 3 hr) the standard furnace pyrolysis of the polymer gave a ceramic of composition 96.6% SiC, 1.7% ZrC and 1.7% Si in 71% yield.

Finally, $(\eta\text{-}C_5H_5)_2Ti(CH_3)_2$ also was an effective catalyst for such crosslinking of the $[(CH_3SiH)_x(CH_3Si)_y]_n$ polysilanes. Its use at room temperature, at reflux or on UV irradiation in hexane solution gave green solid products that were less soluble than those obtained when the zirconium-based catalysts were used. Standard furnace pyrolysis of one such product gave a 71% yield of a black ceramic product of composition 94.8% SiC, 1.2% TiC and 3.9% Si (by weight).

It is clear that in these zirconium and titanium cyclopentadienyl complex-catalyzed reactions of the $[(CH_3SiH)_x(CH_3Si)_y]_n$ polysilanes we are dealing with a unique, unanticipated crosslinking process whose consequences are more far-reaching than merely an increase in ceramic pyrolysis yield. To our knowledge, this is the first example of such a dramatic change in the composition of the ceramic pyrolysis product when a preceramic polymer is subjected to a catalytic chemical treatment.

When I was asked by Dr. Wendell Rhine to give this talk and write this paper, he asked me to consider the following questions with regard to polymer pyrolysis as a route to ceramics.

1) What is the current state of the art?
2) What do we know that is based on scientific principles?
3) What do we need to know to move forward?
4) Can precursors be designed using scientific principles to produce materials with controlled properties?

I shall try to answer these questions, now that I have given a general discussion of this area, followed by some examples from our recent research.

As far as the *synthesis* of the polymers is concerned, I think our *general* understanding of what is needed is good. The *initial* goal, a polymer that is soluble or fusible, whose pyrolysis gives in high yield a ceramic residue of a desired elemental composition, has been attained in one way or another by a number of research groups around the world. Most of this synthetic work is based on known small-molecule chemistry which can be applied to the preparation of polymeric systems. Reproducible attainment of a desired molecular weight and the desired rheological properties still is a problem.

A major problem in the *chemistry* of preceramic polymers is their characterization. There seems to be no really satisfactory method to determine their absolute molecular weights. In most cases, the molecular weights of successful preceramic polymers are not high, generally under 3000 daltons. This is too high for useful application of cryoscopy. Gel permeation chromatography has been applied widely, but there is the question of what the numbers really mean when the reference polymer is a structurally unrelated polystyrene. The "structure" of a nonuniformly crosslinked network polymer is a question without an answer. Infrared spectroscopy and proton and multinuclear NMR spectroscopy, in favorable cases, will tell what

constituent groups are present, but since there is no regular structure, one can only write a "composite structure" (as in Figure 1).

The *chemistry* of the pyrolysis of preceramic polymers can be investigated by various techniques and is reasonably well understood. What volatiles are given off as the temperature is increased can be studied by TGA/FTIR and TGA/MS. Solid state NMR and diffuse reflectance FTIR spectroscopy can be used to study the amorphous pyrolysis residues (and XRD after crystallization has occurred). Solid state NMR is particularly useful in the study of phase development and phase crystallization of the initially amorphous ceramic obtained. Also reasonably well understood is the chemistry that occurs when a reactive gas stream (such as ammonia) is used in the pyrolysis of the polymer.

The connection between the chemistry and the ceramics issues needs much better understanding. How, for instance, does the microstructure of the ceramic produced in the pyrolysis of a polymer depend on the constitution of the polymer (i.e., the nature and connectivity of its chemical "building blocks" and its physical nature (particle size, etc.)? How does it depend on the pyrolysis procedure used? What seems to be "good" chemistry (with regard to the requirements discussed above) does not guarantee "good" ceramics. How can the chemistry be changed to give the desired microstructure and properties? What is the "ideal" microstructure for a given application?

I am a chemist, and I shall leave further discussion of the many ceramics issues associated with the preparation of ceramics by polymer pyrolysis to the ceramists. Not all of them are well understood.

As noted by authors of recent reviews of this field [8e,f], the preparation of ceramics by polymer pyrolysis has gotten off to a good start, but the technology still is in its infancy. A much better understanding of scientific principles, especially at the chemistry/ceramics interface, is required. Close collaboration between the chemists, ceramists and end-users involved is essential to make this technology a scientific and commercial success. Noteworthy are the long-term efforts that have been devoted to the design and synthesis of organosilicon preceramic polymers and their applications in the development of advanced ceramic technology at the Dow Corning Corporation. These have involved just such a collaboration. As that work has shown, considerable patience and considerable investment on the part of management and, in that instance, also of the government, has been required. However, progress, especially in recent years, has been good and successful applications seem to be in sight [28].

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